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- (58) Field of search
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- (71) Applicant
 Norwood Industries Inc
 100 North Marshall
 Road
 Malvern
 Pennsylvania 19355
 United States of
 America

- (72) Inventor
 John Richard McCartney
 (74) Agents
 J Miller and Co
 Lincoln House
 296-302 High Holborn
 London WC1V 7JH

- (54) Aqueous polyurethane composition and method of preparing composite sheet material therefrom

- (57) An aqueous polyurethane composition capable of coagulation by the application of heat thereto comprises an aqueous polyurethane dispersion having anionic groups covalently bonded to the polymer chain and solubilised by the addition of a cationic compound which forms a salt with the anionic group. The polyurethane composition also includes a compound which, when heated in an aqueous solution, gen-

erates acid which causes displacement of the cationic compound from the covalently bonded anionic groups. The compound is suitably sodium or potassium silicofluoride. The polyurethane composition may additionally or alternatively comprise an amount of borax to stabilise the pH of the polyurethane dispersion.

A composite sheet material is formed by impregnating a porous substrate with the polyurethane composition and heating the porous substrate to generate acid causing coagulation of the polyurethane dispersion in the porous sheet material. The impregnated substrate is then dried. The substrate may be a woven or non-woven fabric, a needled batt, a spun-bonded sheet or a waterleave.

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SPECIFICATION

Aqueous polyurethane composition, method of preparing composite sheet material therefrom and composite sheet material prepared thereby

This invention relates to aqueous polyurethane compositions, to methods of preparing composite sheet material therefrom and to composite sheet material prepared thereby.

Resin impregnated sheet materials such as cloth, batts, waterleaves and the like are well-known. These resin impregnated sheet materials are useful for a number of purposes including imitation leather in the form of vinyls and the like, structural sheet materials such as conveyor belts and similar products.

Known methods of impregnating a particular web involve the impregnation or coating of a porous material with a polymeric resin such as a polyurethane, vinyl or a similar material. Polyurethanes have met with wide acceptance as a coating or impregnating composition due to their capability of wide variation in chemical and physical properties, particularly their flexibility and chemical resistance. Several techniques have been employed to impregnate the porous sheet material with a polymeric resin. One such technique involves the use of a polymeric resin in an organic solvent system wherein the sheet material is dipped in the solution and the solvent is removed therefrom. These solvent systems are undesirable since the solvent, in many cases, is toxic and must either be recovered for reuse or be discarded. These solvent systems are expensive and do not necessarily provide a desirable product since upon evaporation of the solvent from the impregnated porous sheet material, the resin tends to migrate to provide a non-homogenous impregnation of the porous sheet material resulting in resin richness toward the surface of the sheet material rather than uniform impregnation.

In order to alleviate the problems with solvent systems, certain aqueous polymeric systems have been proposed. In forming impregnated sheet materials by impregnation with aqueous polymers the aqueous portion must be removed. Heat is required for this and migration of the polymer to the surface of the impregnated sheet material is encountered.

In one method of combining polyurethane solutions with porous substrates a polymer is applied in an organic solvent to a substrate, such as a needle punched polyester batt. The polymer-substrate composite is subsequently bathed with a mixture of organic solvent for the polymer and a non-solvent for the polymer that is at least partially miscible with the solvent until the layer is coagulated into a cellular structure of interconnected micropores. The solvent is removed from the coating layer along with the non-solvent to pro-

duce a solvent free microporous layer. Although this process yields acceptable properties for a polyurethane impregnated fabric, it has the disadvantage of an organic solvent system particularly when high performance polyurethanes are utilised which require relatively toxic and high boiling solvents. An example of this method is disclosed in U.S. Patent Specification No. 3 208 875.

In another method, polyurethane dispersions in organic vehicles have been proposed and used to coat porous substrates such as is disclosed in U.S. Patent Specification No. 3 100 721. In this system a solution is applied to a substrate and coagulated by further addition of a non-solvent for the polymer. Although this approach has been used with some success, it involves two major limitations: (1) the vehicle of the solution is substantially organic since relatively small amounts of non-solvent, preferably water, are needed to form a dispersion; and (2) there is a narrow useful range of added non-solvent so that reproducible results are difficult to obtain. One particularly useful method of preparing composite sheet material by impregnating a porous substrate is disclosed in U.S. Patent Specification No. 4 171 391. In this system a porous sheet material is impregnated with an aqueous ionic dispersion of a polyurethane and the impregnant is coagulated therein. The impregnated sheet material is then dried to form a composite sheet material.

In one improvement over the method disclosed in U.S. Patent Specification No. 4 171 391, fibrous needled batts are fully impregnated with a polyurethane dispersion and coagulated by dipping the impregnant in an aqueous solution of acid such as acetic acid. This improved method is more fully disclosed in British Patent Specification No. A2 085 043.

Although the known methods described in the aforementioned U.S. Patent Specification No. 4 171 391 and British Patent Specification No. A 2 085 043 are successful in alleviating solvents in impregnating porous sheet materials with polyurethanes, a disadvantage in these processes arises in the coagulation step. The coagulation in these processes requires that the porous sheet material impregnated with polyurethane dispersion be contacted with an aqueous solution of a counterion. Thus, the impregnant must be washed free of the excess counterion prior to drying to form the composite sheet material. Further, these counterions can be supplied by low molecular weight organic acids such as acetic acid, which can add an objectionable odour to the final product and also adds expense thereto. Further, in these prior art processes the coagulation rate is determined by the rate of diffusion of the coagulating agent, such as aqueous acid, into the saturated sheet material and subsequent diffusion of the products

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of coagulation in the washing step. In thicker felt products, such as 6.4 mm (0.25 inch) or greater, contact times as long as 30 minutes may be required to effect coagulation. Thus, it is desirable to reduce the time of coagulation.

The present invention seeks to provide a method of preparing a composite sheet material which method simplifies coagulation of polyurethane dispersions in porous sheet materials. Moreover, the present invention seeks to provide an aqueous polyurethane composition where coagulation of the polyurethane dispersion in the porous sheet material is simplified.

According to one aspect of the present invention there is provided an aqueous polyurethane composition capable of coagulation by the application of heat thereto comprising: an aqueous anionic polyurethane dispersion having anionic groups covalently bonded to the polymer chain and solubilised by the addition of a cationic compound which forms a salt with the anionic group; and a compound which, when heated in an aqueous solution, generates acid which displaces the cationic compound from the covalently bonded anionic group.

According to another aspect of the present invention, there is provided a method of preparing composite sheet material comprising: impregnating at least a portion of a porous substrate with a polyurethane composition as recited in the preceding paragraph; heating the impregnated substrate to generate said acid and coagulate the polyurethane dispersion; and drying said impregnated substrate to form a composite sheet material.

According to a further aspect of the present invention, there is provided a composite sheet material when prepared by the method recited in the preceding paragraph.

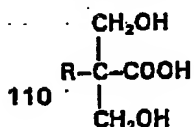
According to yet another aspect of the present invention there is provided a polyurethane composition comprising an aqueous anionic polyurethane having anionic groups covalently bonded to the polymer chain and solubilised by the addition of a cationic compound which forms a salt with the anionic group; and a sufficient amount of borax to stabilise the pH of the polyurethane dispersion.

The polyurethanes useful in the practice of the present invention are those recognised in the art as ionically water dispersible. These dispersions are in contrast with emulsified isocyanate copolymers such as those disclosed in U.S. Patent Specification No. 2 968 575 and prepared and dispersed in water with the aid of detergents under the action of powerful shearing forces. Emulsified polyurethanes have the disadvantage that a detergent must be used to form the emulsion and such detergent is usually retained in the dried emulsion coating, thus seriously detracting from the overall physical and chemical properties of the

final product. Further, insufficient shearing force results in unstable products, and the material cannot usually be produced in conventional reaction kettles because of the need for a high shearing force.

The preferred method for preparing an aqueous polyurethane dispersion is to prepare polymers that have free acid groups, preferably carboxylic acid groups covalently bonded to the polymer backbone. Neutralization of these carboxyl groups with an amine, preferably a water soluble mono-aminem, affords water dilutability. Careful selection of the compound bearing the carboxylic group must be made because isocyanates, necessary components in any polyurethane system, are generally reactive with carboxylic groups. However, as disclosed in U.S. Patent Specification No. 3 412 054 2,2-hydroxymethyl-substituted carboxylic acids can be reacted with organic polyisocyanates without significant reaction between the acid and isocyanate groups due to the steric hindrance of the carboxyl by the adjacent alkyl groups. This approach provides the desired carboxyl containing polymer with the carboxylic groups being neutralised with the tertiary mono-amine to provide an internal quaternary ammonium salt and hence, water dilutability.

Suitable carboxylic acids and preferably sterically hindered carboxylic acids, are well-known and readily available. For example, they may be prepared from an aldehyde that contains at least two hydrogens in the α position which are reacted in the presence of a base with two equivalents of formaldehyde to form a 2,2-hydroxymethyl aldehyde. The aldehyde is then oxidised to the acid by known procedures. Such acids are represented by the following structural formula:



where R is hydrogen or an alkyl group with up to 20 carbon atoms and preferably up to eight carbon atoms. A preferred acid is 2,2-di-(hydroxymethyl) propionic acid. The polymers with the pendent carboxyl groups are characterised as anionic polyurethane polymers.

The polyurethanes useful in the practice of the present invention more particularly involve the reaction of di- or polyisocyanate and multiple, reactive hydrogen-containing compounds suitable for the preparation of polyurethanes. Such diisocyanates and reactive hydrogen-containing compounds are more fully disclosed in U.S. Patent Specifications Nos. 3 412 034 and 4 046 729. Further, the process for preparing such polyurethanes is known, for example from the aforementioned Patent Specifications. In accordance with the

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present invention, aromatic, aliphatic and cycloaliphatic diisocyanates or mixtures thereof can be used. Such diisocyanates, for example, are tolylene-2,4-diisocyanate; tolylene-2,6-diisocyanate; metaphenylene diisocyanate; biphenylene-4,4'-diisocyanate; methylenebis (4-phenyl isocyanate); 4-chloro-1,3-phenylene diisocyanate; naphthylene-1,5-diisocyanate; tetramethylene-1,4-diisocyanate; hexamethylene-1,6-diisocyanate; decamethylene-1,10-diisocyanate; cyclohexylene-1,4-diisocyanate; methylenebis (4-cyclohexyl isocyanate); tetrahydronaphthylene diisocyanate; isophorone diisocyanate and the like. Preferably, arylene and cycloaliphatic diisocyanates are used most advantageously in the practice of the present invention.

Characteristically, arylene diisocyanates encompass those in which the isocyanate group is attached to an aromatic ring. The most preferred isocyanates are the 2,4 and 2,6 isomers of tolylene diisocyanate and mixtures thereof, due to their ready availability and their reactivity. Further, the cycloaliphatic diisocyanates used most advantageously in the practice of the present invention are 4,4'-methylenebis (cyclohexyl isocyanate) and isophorone diisocyanate.

Selection of the aromatic or aliphatic diisocyanates is predicated upon the final end use of the particular material. As is well recognised by those skilled in the art, aromatic isocyanates may be used where the final product is not excessively exposed to ultraviolet radiation which tends to yellow such polymeric compositions; whereas aliphatic diisocyanates may be more advantageously used in exterior applications and have less tendency to yellow upon exposure to ultraviolet radiation. Although these principles form a general basis for the selection of a particular isocyanate to be used, aromatic diisocyanates may be further stabilised by known ultraviolet stabilisers to enhance the final properties of the composite sheet material. In addition, antioxidants may be added to improve the characteristics of the final product. Typical antioxidants that may be used are the thioethers and phenolic antioxidants such as 4,4'-butylidenebis-meta-cresol and 2,6-di-tert-butyl-paracresol.

The isocyanate is reacted with the multiple reactive hydrogen-containing compounds such as diols, diamines, or triols. In the case of diols or triols, they are typically either polyalkylene ether or polyester polyols. A polyalkylene ether polyol is the preferred active hydrogen-containing material for formulation of the polyurethane. The most useful polyglycols have a molecular weight of 50 to 10,000 and in the context of the present invention, the most preferred is from about 400 to 7,000. Further, the polyester polyols improve flexibility proportionally with the increase in their molecular weight.

Examples of polyether polyols are, but not

limited to, polyethylene ether glycol, polypropylene ether glycol, polytetramethylene ether glycol, polyhexamethylene ether glycol, polyoctamethylene ether glycol, polydecamethylene ether glycol, polydodecamethylene ether glycol and mixtures thereof. Polyglycols containing several different radicals in the molecular chain, such as, for example, the compound $\text{HO}(\text{CH}_2\text{OC}_n\text{H}_2\text{O})_n\text{H}$ where n is an integer greater than one, can also be used.

The polyol may also be a hydroxy terminated or hydroxy pendent polyester which can be used instead or in combination with polyalkylene ether glycols. Exemplary of such polyesters are those formed by reacting acids, esters or acid halides with glycols. Suitable glycols are polymethylene glycols such as ethylene, propylene, tetramethylene or decamethylene glycol; substituted methylene glycols such as 2,2-dimethyl-1,3-propane diol, cyclic glycols such as cyclohexanediol and aromatic glycols. Aliphatic glycols are generally preferred when flexibility is desired. These glycols are reacted with aliphatic cycloaliphatic or aromatic dicarboxylic acids or lower alkyl esters or ester forming derivatives to produce relatively low molecular weight polymers, preferably having a melting point of less than about 70°C and a molecular weight like those indicated for the polyalkylene ether glycols. Acids for preparing such polyesters are, for example, phthalic, maleic, succinic, adipic, suberic, sebacic, terephthalic and hexahydrophthalic acids and the alkyl and halogen substituted derivatives of these acids. In addition polycaprolactone terminated with hydroxyl groups may also be used.

One particularly useful polyurethane is the crosslinked polyurethane system which is more fully disclosed in British Specification No. A2 031 920.

The cationic compounds useful in the practice of the present invention are bases capable of forming salts with an anionic group covalently bonded to the polymer chain. The cationic compounds are amines and preferably, water soluble amine such as triethyl amine, tripropyl amine, N-ethyl piperidine etc.

If the final composite sheet material is to be flexible, the polyurethane polymer must behave in an elastomeric manner. The desired elastomeric behaviour would generally require about 25 to 80 percent by weight of a long chain polyol (i.e. 700 to 2,000 eq. wt) in the polymer. The degree of elongation and elasticity may vary widely from product to product depending upon the desired properties of the final product.

In forming polyurethanes useful in the practice of the present invention, the polyol and a molar excess of diisocyanate are reacted to form isocyanate terminated polymer. As will be appreciated reaction conditions and reaction times and temperatures are variable within the context of the particular isocyanate

and polyol utilised. It will be recognised that reactivity of the ingredients involved requires the balance of reaction rate with undesirable secondary reactions leading to colour and molecular weight degradation. Typically, the reaction is carried out with stirring at about 50°C to about 120°C for about one to four hours. To provide pendent carboxyl groups the isocyanate terminated polymer is reacted with a molar deficiency of dihydroxy acid for one to four hours at 50°C to 120°C to form isocyanate terminated prepolymer. The acid is desirably added as a solution, for example, in N-methyl-1,2-pyrrolidone or N-N-dimethylformamide. The solvent for the acid will typically be no more than about 5% by weight of the total charge in order to minimize the organic solvent concentration in the polyurethane composition. After the dihydroxy acid is reacted into the polymer chain, the pendent carboxyl groups are neutralised with an amine at about 58°C to 75°C for about twenty minutes and chain extension and dispersion are accomplished by addition to water with stirring. A water soluble diamine may be added to the water as an additional chain extender. The chain extension involves the reaction of the remaining isocyanate groups with water to form urea groups and further polymerize the polymeric material with the result that all the isocyanate groups are reacted by virtue of the addition to a large stoichiometric excess of water. It is to be noted that the polyurethane compositions of the present invention are thermoplastic in nature, i.e. not capable of extensive further curing after formation except by the addition of an external curing agent. Preferably, no such curing agent is added to form the composite sheet material.

Sufficient water is used to disperse the polyurethane at a concentration of 5 to 50 percent by weight, preferably 5 to 40 percent by weight and more preferably 10 to 40 percent by weight and a dispersion viscosity in the range of 10 to 5,000 centipoise and preferably 10 to 1000 centipoise. Viscosity may be adjusted in accordance with the particular impregnation properties desired and by the particular polyurethane dispersion which are all dictated by the characteristics of the final product. It should be noted that no emulsifiers or thickeners are required for the stability of polyurethane dispersions.

It will be appreciated that the polyurethane dispersions may be modified according to end product uses, for example, by the addition of colouring agents, compatible vinyl polymer dispersions, ultraviolet filtering compounds, stabilisers against oxidation, and by blending polyurethane dispersions of different compositions.

The characterisation of the polyurethane dispersions prepared in accordance with the present invention is done by measurements of non-volatile content, particle size, viscosity

measurements and by stress strain properties on strips of cast film.

The concentration range useful in the practice of the present invention is governed by the desirable percent add on of polymer into the porous sheet material.

Whilst the viscosity is generally in the range from 10 to 1000 centipoise low viscosity, relative to that of identical polymers at the same solids level in organic solvent polymer solutions, assists rapid and complete penetration of the aqueous dispersion. Useful polyurethanes will, in contrast, generally have viscosities of several thousand centipoise ranging as high as 50,000 centipoise at concentrations of 20 to 30%.

Particle size, as a useful measure of stability, may be measured by light scattering. Useful polyurethane dispersions having non-settling characteristics will have particles of a diameter of less than 1 micron.

Porous substrates useful in the practice of the present invention include woven and knit fabrics, felts, and nonwovens, such as spun-bonded sheets, needled batts, and water-leaves. Suitable substrate fibres are natural fibres, particularly cotton (all-cotton and cotton blends with synthetics such as polyester and nylon), and less desirably wool synthetic fibres such as polyester, nylon, acrylics, modacrylics and rayons. The fibres may be straight or crimped, continuous filament or staple, or of papermaking length. Naturally, choice of fibre, type of substrate and its construction, and weight/unit area will be made on the basis of cost, end-use requirements, and other considerations commonly recognised in the textile and coated fabric industries, but only contingent on the particular end use for the composite.

In a method according to the present invention the substrate may be impregnated with polyurethane polymer from about 5% to about 80% of the total composite weight, preferably in the range of 15 to 80%. Thus, the properties of the substrate will strongly affect the properties of the composite sheet material. Property measurements pertinent to shoe and upholstery uses on the finished sheets include tensile strength, tear strength, and bias elongation.

Because the substrate is porous, the aqueous polyurethane composition permeates the pores of the substrate at a rate controlled by the viscosity of the aqueous polyurethane composition and the hydrophilic characteristics of the particular substrate used. Thus, any of the methods used in the coated fabric industry as previously discussed are suitable for impregnating the substrate.

Polyurethane compositions according to the present invention are prepared by admixing the aqueous polyurethane dispersion with a compound which, when heated in an aqueous solution, generates acid which displaces the

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cationic compound from the covalently bonded anionic group.

The compounds which, when heated, generate acid are preferably salts of hydrofluoro-silicic acid. Exemplary of such salts are, but not limited to, lithium silicofluoride; sodium silicofluoride; potassium silicofluoride; ammonium silicofluoride; rubidium silicofluoride; caesium silicofluoride; magnesium silicofluoride; calcium silicofluoride; barium silicofluoride; cupric silicofluoride and manganous silicofluoride. Preferably, either potassium silicofluoride or sodium silicofluoride is used, the latter being preferred.

15 In a preferred method of preparing the polyurethane compositions according to the present invention sodium or potassium silicofluoride salt is masterbatched with 0.02 to 0.2 N aqueous alkali metal hydroxide (either sodium or potassium hydroxide corresponding to the respective silicofluoride) and a dispersion stabiliser such as, for example, clay. To assist the dissolution of the sodium silicofluoride, it is ball milled to about 400 mesh with the aqueous alkali metal hydroxide. The polyurethane dispersion is buffered to stabilise the pH thereof to insure stability of the dispersion at room temperature subsequent to the addition of silicofluoride. Borax has been found to be an effective buffer in this regard and stabilises the dispersion at a pH of about 8.5 in the range of .1 to .2 molar based upon the aqueous polyurethane composition. It is desirable that the pH dispersion be controlled at about 7 to 9. After the polyurethane dispersion is stabilised with the buffer, a portion of the silicofluoride masterbatch is added in an amount sufficient to provide a stoichiometric excess of silicofluoride anion which causes displacement of the cationic compound from the covalently bonded anionic group.

The porous substrate is then impregnated with the aqueous polyurethane composition at room temperature (i.e. about 20°C). Although decomposition of the silicofluoride in the aqueous polyurethane composition occurs at 20°C, long term stability, i.e. weeks, can be achieved by controlling pH and ionic species in the aqueous polyurethane composition. Methods of effecting stabilisation are known to those skilled in the art of using aqueous silicofluoride systems. Some of these systems are more fully disclosed in Fluorine Chemistry, J. H. Simons, pages 126-182, Academic Press 1950; and Chemical & Engineering News, Vol. 27, 2420 CA, Hampel (1949). Subsequent to impregnation the impregnated substrate is heated to greater than 40°C, and preferably greater than 85°C, which causes the generation of silicofluoride anion which causes displacement of the cation from the bonded anionic group effecting coagulation of the polyurethane from the dispersion into the porous substrate. The coagulation is instantaneous and is dependent on the heat transfer

through the impregnated substrate. The heating can be conducted by contacting the impregnated substrate with water which is heated to the desired temperature, by heating the impregnated substrate in an oven, or by treating the impregnated substrate with microwaves to raise the temperature thereof.

When the impregnated substrate is contacted with heated water, the water may contain a minor amount (less than 1%) of a non-volatile mineral acid such as sulphuric and/or phosphoric acid to immediately coagulate the surface of the impregnated substrate to eliminate any loss of polymer. One additional advantage of using heated water is that it also provides a necessary washing step in the process.

After coagulation, the impregnated substrate is squeezed to remove water and washed again with water if desired. The impregnated substrate is then dried to form the composite sheet material.

The following example is illustrative of the present invention.

90 EXAMPLE

50 parts by weight of sodium silicofluoride were ball milled with 50 parts by weight of 0.1 N NaOH and 1% bentonite clay to about 400 mesh to form a sodium silicofluoride

95 dispersion.

100 parts by weight of the aqueous anionic polyurethane dispersion prepared in accordance with Example 3 of British Specification No. A2 031 820 at 22% total solids was admixed with borax to provide a stabilised dispersion of 0.02 molar $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ at a pH of 8.5. 3.5 parts by weight of the silicofluoride dispersions masterbatch was added to the stabilised dispersion to provide a threefold stoichiometric excess of silicofluoride based upon the anionic groups covalently bonded to the polymer chain. The above polyurethane composition was prepared at room temperature and was stable at room temperature for 72 hours prior to use.

A needled batt which was heat set and had a density of 1200 g/m² composed of polyester, polypropylene and rayon fibres and a thickness of 7.8 mm (0.3 inch) with a bulk density of 0.16 g/cm³ was immersed in the above polyurethane composition. Because the polymeric dispersion had a 22% total solids content, it provided an add on of 120% polyurethane based upon the weight of the batt. The batt, on a continuous basis, was immersed in the polyurethane composition at room temperature until all of the air was expelled from within the batt and the batt was fully impregnated. The surface of the batt was wiped with a straight edge on both sides to remove excess polyurethane composition. The impregnated batt was, on a continuous basis, immersed in a water bath at 70°C for one minute. The water bath had 0.5% H_3PO_4 .

130 Immersion in the water bath completely coag-

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- ulated the polyurethane within the fibre structure. The impregnated batt was squeezed between nip rolls to eliminate water, washed with clear water and squeezed again. The impregnated batt was split into four slices through its thickness and each slice was dried at 149°C to 177°C (300°F to 350°F) in a circulating air oven to form four resin impregnated webs having a bulk density of 0.41 g/cc. The composite sheet material produced in accordance with this Example was comparable to that produced in accordance with Example I of British Specification No. A2 085 043.
- 15 An aqueous polyurethane composition according to the present invention may result in a substantial reduction in coagulation time by using the high diffusion rate of heat through the impregnated substrate to coagulate the polyurethane composition.

CLAIMS

1. An aqueous polyurethane composition capable of coagulation by the application of heat thereto comprising: an aqueous anionic polyurethane dispersion having anionic groups covalently bonded to the polymer chain and solubilised by the addition of a cationic compound which forms a salt with the anionic group; and a compound which, when heated in an aqueous solution, generates acid which displaces the cationic compound from the covalently bonded anionic group.
2. A polyurethane composition as claimed in claim 1 in which said polyurethane dispersion has a solids content of 5 to 50 percent by weight.
3. A polyurethane composition as claimed in claim 2 in which said polyurethane dispersion has a solids content of 10 to 40 percent by weight.
4. A polyurethane composition as claimed in any preceding claim in which said polyurethane dispersion has a viscosity of 10 to 5,000 centipoise.
5. A polyurethane composition as claimed in claim 4 in which said polyurethane dispersion has a viscosity of 10 to 1000 centipoise.
6. A polyurethane composition as claimed in any preceding claim in which said polyurethane dispersion is a crosslinked polyurethane dispersion.
7. A polyurethane composition as claimed in any preceding claim in which the compound which when heated, in an aqueous solution, generates acid is a salt of hydrofluorosilicic acid.
8. A polyurethane composition as claimed in claim 7 in which said salt of hydrofluorosilicic acid is sodium silicofluoride or potassium silicofluoride.
9. A polyurethane composition as claimed in any preceding claim in which said compound which, when heated in an aqueous solution, generates acid is present at a level wherein there is a stoichiometric excess of acid based upon the anionic covalently bonded groups.
10. A polyurethane composition as claimed in any preceding claim including a buffer to maintain the pH of said polyurethane dispersion at 7 to 9.
11. A polyurethane composition as claimed in claim 10 in which said buffer maintains the pH of said polyurethane dispersion at about 8.5.
12. A polyurethane composition as claimed in claim 10 or 11 in which said buffer is borax.
13. A polyurethane composition as claimed in any preceding claim including an alkali hydroxide.
14. A polyurethane composition as claimed in claim 1 and substantially as herein described.
15. A method of preparing composite sheet material comprising: impregnating at least a portion of a porous substrate with a polyurethane composition as claimed in any preceding claim; heating the impregnated substrate to generate said acid and coagulate the polyurethane dispersion; and drying said impregnated substrate to form a composite sheet material.
16. A method as claimed in claim 15 in which said composite sheet material is comprised of 5 to 80 percent by weight polyurethane polymer.
17. A method as claimed in claim 15 or 16 in which the substrate is a woven fabric, a non-woven fabric, a needled batt, a spun-bonded sheet or a waterleave.
18. A method as claimed in any of claims 15 to 17 in which the impregnated substrate is heated to a temperature greater than 40°C to coagulate the polyurethane dispersion.
19. A method as claimed in claim 18 in which said impregnated substrate is heated to a temperature greater than 65°C to coagulate the polyurethane dispersion.
20. A method as claimed in any of claims 15 to 20 in which said impregnated substrate is heated by contact with water.
21. A method as claimed in claim 20 in which said water contains a minor amount of non-volatile mineral acid.
22. A polyurethane composition comprising an aqueous anionic polyurethane having anionic groups covalently bonded to the polymer chain and solubilised by the addition of a cationic compound which forms a salt with the anionic group; and a sufficient amount of borax to stabilise the pH of the polyurethane dispersion.
23. A method of preparing composite sheet material substantially as herein described with reference to the Example.
24. A composite sheet material when prepared by the method claimed in any of claims 15 to 23.

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